SUPPORTING INFORMATION

Chemical transformations at the nanoscale: nanocrystalseeded synthesis of β -Cu₂V₂O₇ with enhanced photoconversion efficiencies

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EXPERIMENTAL DETAILS

MATERIALS

Copper (I) acetate (CuOAc, 97%), hexane (anhydrous, 95%) was purchased from TCI Deutschland GmbH. Vanadium (V) oxide (V_2O_5 , 99.9%), toluene (anhydrous), Dimethylformamide (DMF, anhydrous), Acetonitrile (ACN, anhydrous), and vanadium (III) chloride (VCl₃, 99%) were purchased from abcr GmbH. Trioctylamine (TOA, 98%), oleylamine (OLAM, 70%), tetradecylphosphonic acid (TDPA, 97%), trimethyloxonium tetrafluoroborate (Me₂OBF₄, 95%), ethanol (anhydrous), trioctylphosphine (TOP, 90%), copper (I) chloride (CuCl, 99.99%), copper (II) oxide (CuO, 98%), and copper (II) nitrate hydrate (Cu(NO₃)₂·xH₂O, 99.999%) were purchased from Sigma-Aldrich and used as received. Ethylene glycol (99.5%) was purchased from Roth AG.

COLLOIDAL SYNTHESIS OF THE COPPER NANOCRYSTAL (NC) SEEDS.

6nm Cu NCs were synthesized by modifying the procedure from Hung et al.¹10 mL of TOA were introduced into a threenecked flask and kept under vacuum for 30 min. This step was followed by heating under nitrogen flow at 130°C for 30 minutes. Following the cooling of TOA to room temperature, 1 mmol of CuOAc and 0.5 mmol of TDPA were added the flask under vigorous stirring. The solution was then heated to 180°C and maintained at this temperature for 30 minutes followed by one final heating step to 300°C and 30 minute soak. The solution was naturally cooled to 60°C and transferred to a vial under N₂ flow. Anhydrous ethanol was added for washing and the solution centrifuged at 6000 rpm for 20 minutes. The precipitate was dispersed in hexane and kept under N₂ in glovebox. A 0.2 M stock solution of 6nm Cu NC was used as seeds to grow bigger 11nm and 14 nm Cu NCs.

11 nm Cu NCs were synthesized starting from the 6nm Cu NCs. 10 mL of TOA were degassed in a three-necked flask at 130°C under N_2 flow for 30 minutes and cooled naturally to room temperature. 500 µL of 6 nm Cu NC from the 0.2M stock solution in hexane was added to the flask under N_2 flow, and the solution heated to 270°C. 1 mmol of CuOAc and 0.5 mmol of TDPA were dissolved in 3 mL of TOA at 150°C and injected into the flask using a syringe pump at a flow rate of 0.3 mL·min⁻¹ when the flask temperature reached 250°C. The solution was kept at 270°C for 20 minutes and naturally cooled to room temperature. The same extraction and washing procedure as reported earlier was used. The precipitate was dispersed in hexane and kept under N_2 in glovebox.

14 nm Cu NCs were synthesized starting from the 6nm Cu NCs. 10 mL of TOA were degassed in a three-necked flask at 130°C under N_2 flow for 30 minutes and cooled naturally to room temperature. 250 µL of 6 nm Cu NC from the 0.2M stock solution in hexane was introduced into the flask under a N_2 flow and the solution heated to 270°C. 5 mmol of CuOAc and 2.5 mmol of TDPA were dissolved in 9 mL of TOA at 150°C and injected into the flask at a flow rate of 0.3 mL min⁻¹ when the flask temperature reached 250°C. The solution was kept at 270°C for 20 minutes and naturally cooled to room temperature.

The same extraction and washing procedure as earlier reported was used. The precipitate was dispersed in hexane and kept under N_2 in glovebox.

40 nm Cu NCs were synthesized by modifying the procedure reported by Lu et al. ² 18 mL of OLAM were degassed at room temperature in a 3-necked flask for 1 hour. 0.2 mmol of CuCl was dissolved in 0.5 mL TOP at 200°C under continuous stirring for 2 hours. OLAM was heated to 335°C under N₂ flow followed by gradual injection of mixture of CuCl and TOP. The solution was kept at 335°C for 40 minutes followed by rapid cooling of the flask to 230°C with N₂ flow followed by quenching of solution with water at 230°C. The reaction solution was then transferred to a vial under N₂ flow followed by washing with toluene and centrifugation at 6000 rpm for 20 minutes. The precipitate was dispersed in hexane and kept under N₂ in glovebox.

60 nm Cu NCs were synthesized by modifying the procedure from Huang et al.¹ 10 mL of TOA were degassed in a 3-necked flask at 130°C under N_2 flow for 30 minutes and cooled naturally to room temperature. 1 mmol of CuOAc and 2 mmol of TDPA were introduced into the flask under vigorous stirring. The solution was then heated to 180°C and maintained at this temperature for 30 minutes followed by quick heating to 270°C and maintained for 30 minutes. The solution was naturally cooled to 60°C and transferred to a vial under N_2 flow. Anhydrous ethanol was added for washing and the solution was centrifuged at 6000 rpm for 20 minutes. The precipitate was dispersed in hexane and kept under N_2 in glovebox.

70 nm Cu NCs were synthesized by modifying the procedure reported by Lu et al.² 18 mL of OLAM were degassed at room temperature in a 3-necked flask for 1 hour. 0.2 mmol of CuCl were dissolved in 2.0 mL TOP at 200°C under continuous stirring for 2 hours. OLAM was heated to 335°C under N₂ flow followed by gradual injection of mixture of CuCl and TOP. The solution was kept at 335°C for 40 minutes followed by rapid cooling of the flask to 230°C with N₂ flow followed by quenching of solution with water at 230°C. The reaction solution was then transferred to a vial under N₂ flow followed by washing with toluene and centrifugation at 6000 rpm for 20 minutes. The precipitate was again dispersed in hexane and kept under N₂ in glovebox.

DETERMINATION OF THE NC SOLUTION CONCENTRATION.

 $50 \ \mu$ l of the as-synthesized Cu NC solutions were deposited in the aluminium pan. Thermogravimetric measurements were performed in the TGA Q500 with the flow of air maintained at 15 mL min⁻¹. The samples were heated with a heating ramp of 10° C min⁻¹ to 600° C during which the Cu NCs are oxidized to CuO. The final mass of the material was assumed as CuO to determine the concentration of Cu NCs.

SEM

SEM images were acquired on a FEI Teneo 200 FEG Analytical Scanning Electron Microscope using a beam energy of 2 keV.

TEM

TEM images were acquired on a FEI Tecnai Spirit using a beam energy of 200 kV, equipped with a Gatan camera. Samples were drop-casted on a copper TEM grid (Ted Pella, Inc) prior to imaging. Size statistics was performed using the software ImageJ and counting at least 200 particles per sample.

RAMAN SPECTROSCOPY

Raman spectra were recorded using a confocal Raman microscope (Renishaw inVia Raman microscope) with a 532 nm laser source of maximum power of 45W. The measurements were performed with a 100x objective in the Raman microscope with 5% of laser power. The spectral positions were calibrated by the characteristic Si phonon peak at 520.7 cm⁻¹.

XRD

X-ray diffraction data was acquired on a Bruker D8 Discover diffractometer with a non-monochromated Cu K α source equipped with a Lynxeye 1-D detector. A corundum standard (NIST 1976b) was used as a reference to determine the instrumental broadening in order to estimate the size-induced broadening of XRD peaks.

ATR-FTIR

Attenuated total reflectance Fourier transform infrared spectroscopy was performed using a Perkin Elmer instrument Spectrum 100. Samples were prepared on silicon substrates, and measured with a resolution of 4 cm⁻¹. The background was obtained on the bare silicon substrate.

IN-SITU XRD



The measurements were carried out with a custom-made heating cell implemented into a Bruker D8 Discover diffractometer. For thin films, the precursor solutions were deposited onto Si substrates. Powder samples were co-ground in an agate mortar, and deposited on Si wafers. A uniform layer was achieved by adding a drop of ethanol, once the powder mixture was deposited on the substrate. The chamber of the cell was at all times kept under dry air, flowing at 10 slph. Heating was achieved by passing electrical current through a Ni-Cr or stainless steel, 0.1 mm thick, strip, attached to a compensating spring mechanism to minimize thermal dilatation effects. Temperature was controlled by a PID controller connected to a thermocouple placed underneath the heating strip, directly below the sample. Before each series of experiments, the position of the sample was verified by measuring the thermal expansion of a MgO reference powder deposited on a Si wafer. Temperature calibration was carried out up to 600°C, by heating the MgO powder and comparing the refined lattice parameters with literature data.³ The results were confirmed by placing a thermocouple on the surface of the Si wafer. In the experiment shown in Figure 4, the heating to 350°C was performed in 135 minutes (around 25°C/min). During this time, six patterns were collected in the theta range between 20 and 40°. No influence of the heating ramp was detected. The same conditions were used for the experiments in Figure S4 B), D), F). For the experiments in Figure S4 A), C), E), the heating ramp was adjusted based on the conversion kinetics of the sol gel precursors, of the bulk powders and of the pure vanadium precursor, respectively. The heating ramp can be extracted from the y-axis.

XRD RIETVELD REFINEMENT

Data analysis was done using Topas.⁴ Patterns were fitted using structures available in the PDF 4+ ICDD 2018 database: V_2O_5 Pmmn (PDF No. 00-041-1426), β -Cu₂V₂O₇ C12/c1 (PDF No. 01-076-2820), CuV₂O₆ C1 (PDF No. 00-045-1054). The alumina standard NIST SRM1976b was used to determine instrumental peak broadening for size analysis. The domain sizes were determined from the volume weighted mean column height using the macro LVol_FWHM_CS_G_L in Topas. A model based on spherical harmonics was used to treat errors in intensities arising due to preferential orientation of V₂O₅ (macro spherical_harmonics_(hkl)). Given the low quality of the obtained patterns caused by nanometer size of the grains and by the form in thin films of the samples, the relative errors on the phase composition reported in Table S1 were significant, yet they give us a good trend of changes with the nanocrystal seed size.

UV-VIS SPECTROSCOPY

The transmission and reflectance measurements were recorded on a Perkin Elmer-Lambda 1050 UV/Vis/NIR Spectrophotometer with a D2(Deuterium) lamp for ultraviolet and a WI(halogen) lamp for the visible and infrared range. Measurements were performed with an integrating sphere. The absorption coefficient (α) was calculated from the reflectance and transmittance data using the following equation: $\alpha = -[\ln((\%T+\%R)/100)]/d$ where d was the film thickness which was measured as 1.35 µm using profilometer.

PHOTOELECTROCHEMICAL MEASURAMENTS

The photoelectrodes were prepared on FTO substrate $1.5 \times 1.5 \text{ cm}^2$ using the same procedure described in Experimental section. The obtained films appeared yellow in color with a thickness around 350 nm measured using a profilometer.

Photoelectrochemical performance of photoanodes were evaluated in a typical three-electrode configuration using a SP-200 (BioLogic) potentiostat/galvanostat. The light source was an AM 1.5 solar simulator (ORIEL LCS-100 Series Solar Simulator model) with the illumination intensity adjusted to 100 mW/cm². All illuminated areas were approximately 0.8 cm². Photocurrent measurements were performed in a sodium borate buffer solution (pH 8.2) with 0.1 M sodium sulfite (Na₂SO₃) as a hole scavenger under back illumination. Photocurrents were carried out using a Ag/AgCl (3.5M KCl) reference electrode, all results in this work are presented against the reversible hydrogen electrode (RHE) for ease of comparison with other papers that use electrolytes with different pH conditions. The conversion between potentials vs. Ag/AgCl and vs. RHE is performed using the following equation:

 $E(vs. RHE) = E(vs. Ag/AgCl) + E_{Ag/AgCl}(reference) + 0.0591V* pH$

 $E_{Ag/AgCl}$ (reference) = 0.1976 V vs. NHE at 25 °C

A set of 3 photoelectrodes was tested for each studied photoanode and the average values are reported.

Incident photon-to-current efficiency (IPCE) and absorbed photon-to-current efficiency (APCE) were measured as a function of incident photon energy in a sodium borate buffer (pH 8.2) with 0.1 M sodium sulfite (Na_2SO_3) as a hole scavenger under back illumination. The chronoamperometry measurements were performed at an applied potential of 1.23V vs RHE with 3 different LEDs of illumination wavelengths: 657 nm (1.97 eV) , 526nm (2.36 eV)and 451nm (2.75 eV) The IPCE and APCE was calculated using the following formula:

$$IPCE(\%) = \frac{1240J_{net}}{P\lambda} \times 100$$
$$APCE(\%) = \frac{IPCE}{(1 - R - T)}$$

where J_{net} is the net photocurrent density of the electrode after subtraction of the dark current in $mA. cm^{-2}$, P is the power output by each LEDs in $mW. cm^{-2}$, λ is the illumination wavelength of the LED in nm, R and T are the fractional reflectance and transmission of the films on FTO.

TEM ANALYSIS OF THE COPPER VANADATE FILMS

Sample preparation: 40 μ L of ethanol was dropped on the annealed film deposited on silicon substrate. The sample is then collected by gently scrubbing a carbon coated gold TEM grid on the annealed film. The TEM grid was normally dried in air for TEM analysis. High-resolution TEM imaging was performed on a FEI Tecnai Osiris at 200 kV.



Figure S1 A) XRD pattern of films synthesized from 6nm Cu NC seeds annealed at 350°C, 450°C and 500°C for 2 hours. Monoclinic β -Cu₂V₂O₇ (PDF-01-076-2820), triclinic CuV₂O₆ (PDF-00-045-1054) and V₂O₅ (PDF-00-041-1426) reference patterns are reported. Plane view SEM images of the films synthesized at 350°C(D), 450°C(C) and 550°C(B) showing an increase in grain size. In (C) the presence of V₂O₅ is clearly evidenced by the formation of needle-like grains.



Figure S2 A)XRD patterns and B) Raman spectra of films synthesized from 6nm Cu NC seeds with Cu:V ratio varying from 2 to 0.5, annealed at 350°C for 8 hours. For the XRD analysis, monoclinic β -Cu₂V₂O₇ (PDF-01-076-2820), CuO (PDF no. 01-078-2076) and V₂O₅ (PDF-00-041-1426) reference patterns are reported. For Raman analysis, reference spectra are adapted from Kawada et al.⁵ Both XRD and Raman evidence that Cu:V=1:2 clearly result into an excess of vanadium oxide in the samples and Cu:V=2:1leaves behind unreacted CuO.



Figure S3 Cross-sectional SEM image of a typical β -Cu₂V₂O₇ film synthesized from 6nm Cu NC seeds.



Figure S4 Raman spectra of films synthesized from 6 nm, 11 nm, 14 nm, 40 nm, 60 nm and 70 nm Cu NC seeds. Reference spectra for CuV₂O₆ and β -Cu₂V₂O₇ are from Kawada et al.⁵ The signals corresponding to the Si substrate are indicated as • in the figure. The signal from the V₂O₅ at 1000cm⁻¹ and 692 cm⁻¹ is not detected.

A strong scattering peak was detected at ~902 cm^{-1} which may correspond to the VO₃ stretching in either β -Cu₂V₂O₇ (903 cm^{-1} ,910 cm^{-1})⁶ or CuV₂O₆ (904 cm^{-1}).⁵ Since, β -Cu₂V₂O₇ was measured as the primary component in all the films from XRD, this peak at 902 cm^{-1} most likely corresponds to β -Cu₂V₂O₇. In addition, all the films show peaks at 860 cm^{-1} , 786 cm^{-1} and 389 cm^{-1} which correspond to the VO₃, V-O-V and O-VO₃ bending modes of β -Cu₂V₂O₇, respectively.⁶ The absence of any Raman signal assigned to V₂O₅, which was detected by the Rietveld analysis of the XRD patterns, may be due to the low quantity of V₂O₅ on the films.

Table S1 Phase composition and grain sizes of films synthesized from 6 nm, 11 nm, 14 nm, 40 nm, 60 nm and 70 nm Cu NC seeds as determined from Rietveld refinement and Scherrer analysis of the XRD data shown in Figure 2. The seed diameters were determined through statistical analysis of the TEM images counting 200 particles.

Seed diameter [nm]	β -Cu ₂ V ₂ O ₇ [%]	$V_2O_5[\%]$	$CuV_2O_6[\%]$	Grain size [nm]
6 ± 0.5	98.0 ± 1	2.0 ± 1.0	0	29
11 ± 1	91.0 ± 4	9.0 ± 4.5	0	33
14 ± 1	93.0 ± 3.5	7.0 ± 3.5	0	36
40 ± 5	96 ± 2.0	4.0 ± 2.0	0	39
60 ± 10	79 ± 0.5	1.0 ± 0.5	20 ± 0.5	61
70 ± 7	85 ± 1.5	3 ± 1.5	12 ± 1.5	63



Figure S 5 Two examples of the profile fitting by Rietveld refinement corresponding to films synthesized from A) 6 nm and B) 60 nm NC seeds.



Figure S6 In-situ XRD experiments on: A) mixture of Cu(NO₃)₂·H₂O and VCl₃ molecular precursors in 1:1 Cu:V molar ratio; B) 60 nm Cu NC seeds and VO(acac)₂; C) CuO and V₂O₅ co-grinded powders; D) purely metallic 6 nm Cu NCs ; E) VO(acac)₂ in DMF deposited on a substrate. V₂O₅ (\blacktriangle), β -Cu₂V₂O₇ (\triangledown), CuO (\bullet), α -Cu₂V₂O₇ (\circ), VO(acac)₂ (\blacksquare), CuV₂O₆ (+), Cu₂O (*).

In panel A the sol-gel samples were prepared from molecular precursors, according to the method reported in Guo et al^7 , the initial peak at 28.5 degrees corresponds to one of the precursors. The ternary phase appears between 200°C.

In panel B 60 nm NCs were used as seeds, and the ternary phase is detected after 10 minutes at 350°C.

Powdered samples used in C were prepared by co-grinding CuO and V_2O_5 in an agate mortar. The ternary phases appeared at around 500°C.

In panel D, the not oxygen treated 6 nm Cu NCs sinter while oxidizing to CuO at temperatures as low as 150°C, as evidenced by the sharpening of the diffraction peaks.

Instead panel F shows that the oxygen treatead 6 nm Cu NCs (Cu@Cu₂O) transform into CuO at around 200°C without undergoing substantial sintering as the peaks remain broad.

The measurements in panel E evidence the transformation of $VO(acac)_2$ into V_2O_5 at around 300°C. The reflection at 21 degrees might correspond to a transition phase, which we were not able to assign.



Figure S 7 XRD pattern of 6nm ligand-stripped Cu NCs after surface oxidation. This result is consistent with $Cu@Cu_2O$ as reported by Hung et al.¹



Figure S 8 Comparison between XRD patterns of films synthesized from purely metallic 6nm Cu NC seeds and from surface oxidized 6nm Cu NC (referred to as $Cu@Cu_2O$ NC) seeds mixed with $VO(acac)_2$ in Cu:V=1:1 ratio, which were annealed at 350°C for 8 hour. The sample synthesized from purely metallic Cu seeds clearly show the presence of unreacted CuO.



Figure S 9 FT-IR spectra of VO(acac)₂, of the ligand stripped Cu@Cu₂O NCs and of the precursor solution containing the ligand-stripped Cu@Cu₂O NCs and the VO(acac)₂.

After ligand stripping the surface of the NCs is bare and positively charged. Thus chemical interactions with the $VO(acac)_2$ can be foreseen. The shifts reported in table S2 are indicative of such interactions. The peak assignment in Table S2 is referenced in Nenashev et al.⁸

Table S2 VO(acac) ₂	vibrational shifts	dictated by the	presence of the	Cu@Cu ₂ O NCs.
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	V=O	V-0	С-Н	C-C-C
	[cm ⁻¹]	[cm ⁻¹]	[cm ⁻¹]	[cm ⁻¹]
VO(acac) ₂ in DMF	991	459	786	657
VO(acac) ₂ +Cu@Cu ₂ O NCs in DMF	996	453	780	652



Figure S10 Optical properties of the films. A) Absorbance spectra of a 1.35 µm-thick film of typical β -Cu₂V₂O₇ and a typical 1.35 µm-thick film biphasic β -Cu₂V₂O₇ +CuV₂O₆ films on quartz substrate, measured with an integration sphere as a function of wavelength. B-C) Tauc plots of the same films corresponding to indirect transitions, respectively, along with linear fits for the band gap.



Figure S11 A) J-V curves under dark and illuminated conditions, and B) Net photocurrent density obtained by subtracting the dark current, J_{net} vs V curve of the full set of films synthesized from 6 nm, 11 nm, 14 nm, 40 nm, 60 nm and 70 nm Cu NC seeds measured in a 0.1M sodium borate buffer (pH 8.2) containing 0.1M Na₂SO₃ as hole scavenger, under AM 1.5G, 100 mW cm⁻² illumination (scan rate = 10 mV s⁻¹). C) Plot of the net sulfite oxidation photocurrent J_{net} , calculated by subtracting the dark current at 1.23V vs RHE , as a function of β -Cu₂V₂O₇ grain size. The data points in red represent the biphasic β -Cu₂V₂O₇ + CuV₂O₆ samples. D) J-V curve of a typical β -Cu₂V₂O₇ nanocrystalline film obtained from 6nm Cu NC seeds in a 0.1M borate buffer (pH 8.2) under AM 1.5G, 100 mW cm⁻² illumination (scan rate = 10 mV s⁻¹).

As already commented in the manuscript, the high dark currents are consistent with literature reports about this phase and other phases of copper vanadates when measured in similar conditions.^{7,9–12} While their origin remains to be investigated, they might be indicative of a dark electrochemical reaction occurring between the photoanode surface and the hole scavenger. Thus it is interesting to note in Figure S11A that these background currents increase when going from films synthesized from 6nm seeds to 11nm to 14nm as indication of increased surface area exposed to the hole scavenger. A non-linear dependence is observed for bigger sizes, which suggests that other factors come into place.

Figure S11D reports the J-V curves of β -Cu₂V₂O₇ nanocrystalline film obtained from the 6nm Cu NC seeds in the absence of hole scavenger. In this case the dark current was closer to zero and also the net photocurrent substantially decreased as expected (J_{net} = 1.81 μ A/cm² at 1.23V vs RHE in the absence of the scavenger versus Jnet = 60 μ A/cm² at 1.23V vs RHE in the presence of the scavenger for the film with 26 nm grain size). The sample performed quite poorly as no optimization of film thickness (our films are only 350 nm thick) or surface functionalization with a water oxidation catalyst was performed. Nevertheless these data should be sufficient to demonstrate that the photocurrent values reported in the manuscript are due to photoelectrochemistry as opposed to photoconductivity.



Figure S12 (A) IPCE (circles) and APCE (triangles) data for β -Cu₂V₂O₇ films obtained from 6 nm and 14 nm Cu seeds in sodium borate buffer (pH 8.1) with 0.1 M Na₂SO₃ at 1.23 V vs RHE. The measurements were performed at 3 different wavelength of irradiation (628 nm, 526 nm and 451 nm) using LEDs and the photocurrent obtained was normalized with the power of the LED sources to calculate the IPCE. (B) Corresponding absorbance spectra of the photoelectrodes (350 nm thick) on FTO substrate. The blue, green and red dotted line represent the wavelength of LED irradiation of 451 nm, 526 nm and 628 nm.

The APCE values for the β -Cu₂V₂O₇ films obtained from 6 nm and 14 nm Cu seeds are higher than the already reported values in literature for this stoichiometry of copper vanadate which is in agreement with the higher photocurrent values reported in this study.^{7,12}



Figure S13 Magnification of J-V curves of β -Cu₂V₂O₇ films synthesized from 6 nm, 11 nm, 14 nm and 40 nm Cu NC seeds to determine the onset potential for sulfite oxidation.

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